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Mössbauer spectroscopy of KrF_2 and $KrF_2 \cdot MF_5$ (M = As, Sb)

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Mössbauer spectra of KrF_2 and the recently synthesized compounds α- and β- $[KrF]^+[AsF_6]^-$ and $[KrF]^+[SbF_6]^-$ have been measured using the 9.4 keV transition of ^{83}Kr produced in the decay of an ^{83}RbF source. The results for the values of quadrupole coupling strengths and the isomer shifts indicate that the Kr–F bonding in all compounds studied is very similar. A slight increase of the quadrupole coupling in going from KrF_2 to F–Kr–F–MF_5 can be interpreted in terms of a shortening of the average Kr–F bond length. A very accurate value, $Q_{ex}/Q_{gr} = 1.958 \pm 0.002$ for the ratio of the quadrupole moments of the 9.4 keV state and the ground state has also been derived from the measurements.

I. INTRODUCTION

Since the discovery of noble gas compounds in 1962, the properties of many xenon compounds have been thoroughly investigated by chemical and physical methods.[1] Research on krypton compounds has been less widespread, mainly due to the much greater difficulties in preparing and manipulating samples. Recently, however, the character of Kr–F bonds has been investigated by vibrational[2–7] and nuclear magnetic resonance[4,5] spectroscopy. The only hyperfine interaction investigation so far reported is the Mössbauer study on KrF_2 by Ruby and Selig,[8] who used the 9.4 keV transition in ^{83}Kr in their recoilless gamma resonance experiments on this compound. Their work yielded values for the quadrupole interaction strength, the quadrupole moment ratio Q_{ex}/Q_{gr} of the 9.4 keV state and the ground state of ^{83}Kr, and the isomer shift. From the isomer shift, combined with Hartree–Fock calculations of electron densities at the ^{83}Kr nucleus, a value was derived for the relative change of nuclear radius $\delta R/R$ between the 9.4 keV state and the ground state. The values of Q_{ex}/Q_{gr} and $\delta R/R$ were later recalculated by Kolk[9,10] from the same experimental data.

In the present work we have remeasured KrF_2 under greatly improved experimental conditions as part of a series of Mössbauer investigations of krypton compounds which further included α-$[KrF]^+[AsF_6]^-$, β-$[KrF]^+[AsF_6]^-$ and $[KrF]^+[SbF_6]^-$. These experiments have enabled us to obtain a more accurate value of the quadrupole moment ratio and to relate the structures of these compounds to KrF_2.

II. EXPERIMENTAL

Krypton difluoride was prepared by passing an electric discharge through a 1:1.1 mixture of Kr (British Oxygen Company) and F_2 (Matheson) at −180 °C and ~20 mm Hg pressure. The method was similar to that described by Schreiner *et al.*[11]

The adducts $[KrF]^+[AsF_6]^-$, $[KrF]^+[SbF_6]^-$ were prepared in dried, prefluorinated 0.25 in. o.d. ×0.030 in. wall tetrafluoroethylene/perfluoropropylene copolymer (FEP) tubes as follows:

The adduct α-$[KrF]^+[AsF_6]^-$ was prepared from KrF_2 and AsF_5 under carefully controlled conditions as outlined by Gillespie and Schrobilgen.[4,5] The low-temperature β-modification was obtained by allowing the sample to stand at −78 °C for 24 h.[4,5]

$[KrF]^+[SbF_6]^-$ was obtained by the controlled thermal decomposition of $[Kr_2F_3]^+[SbF_6^-]$ prepared by the interaction of excess of KrF_2 with SbF_5.[5]

In all cases, low-temperature Raman spectroscopy was used to monitor the progress of reactions and to demonstrate the purities of the final products.

The prepared samples were rapidly mixed with dried, prefluorinated Teflon powder in an oxygen-free, nitrogen-filled drybox (Lintott Engineering Limited, Horsham, Essex) at room temperature. The powdered fluoride samples (~30 mg of KrF_2 or 20 mg of the adducts) were each measured out by volume in precalibrated dried aluminium scoops and mixed with known quantities (sufficient to give ~20 mg cm^{-2} at the absorber holder window) of the dried Teflon. The intimate mixtures were rapidly encapsulated in thin-windowed Teflon absorber holders and immediately immersed in liquid nitrogen. The samples were stored under liquid nitrogen, and all subsequent manipulations of the holders were carried out at close to liquid nitrogen temperatures. Since the mixed powders could not be tightly compressed in the absorber holder, the absorbers required judicious shaking and tapping before measurement to achieve a reasonably homogeneous spread of the material.

The compound ^{83}RbF was used as a source of 9.4 keV radiation. The $^{83}Rb(T_{1/2} = 83d)$ activity, which decays to ^{83}Kr by electron capture, was produced in the cyclotron of the Groningen Nuclear Accelerator Institute (K. V. I.) from enriched ^{86}Sr by a $(p, 4n)$ reaction.[12] Activities of the order of 2 mCi were obtained.

All measurements were performed in a liquid helium cryostat at 4.2 K. The 9.4 KeV radiation was detected with a krypton–methane proportional counter. Some of the spectra are shown in Fig. 1. The solid lines through the points represent computer fits, to be dis-

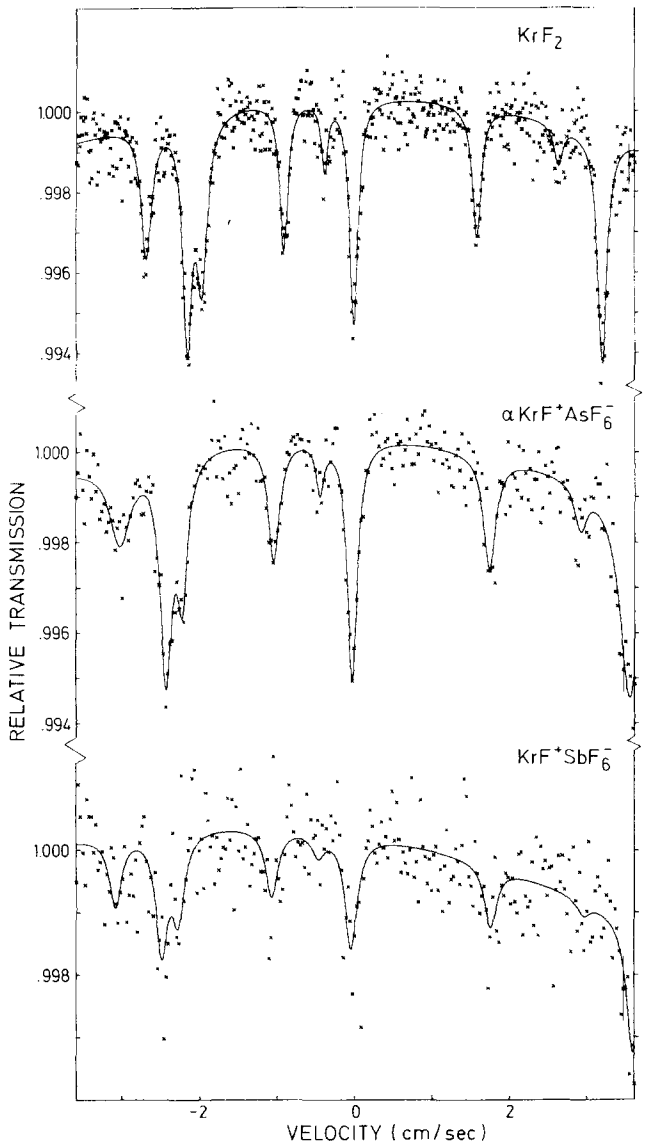

FIG. 1. Mössbauer spectra of three krypton compounds used as absorbers (^{83}Kr thickness mg/cm^2) taken at liquid helium temperature with a source of ^{83}RbF.

cussed in the next section. The velocity range of these spectra encompasses 9 out of the 11 lines of the quadrupole pattern of the $\frac{7}{2}$–$\frac{9}{2}$ transition in ^{83}Kr. Spectra which include only the three innermost lines were also taken for KrF_2 and α-$[KrF]^+[AsF_6]^-$. The velocity scale was calibrated with a ^{57}Fe spectrum, using a $^{57}CoRh$ source and an enriched ^{57}Fe metal absorber. Calibration runs were made at room temperature before and after the krypton measurements.

III. RESULTS

The spectra were least squares fitted for an axially symmetric quadrupole interaction, where the positions of the spectral components are related by the expression

$$\nu_{m^*,\,m} = \tfrac{1}{4}e^2qQ_{gr}(c/E_\gamma)[(Q_{ex}/Q_{gr})\,C(m^*, I^*) - C(m,\, I)] + \delta \tag{1}$$

where $C(m, I) = [3m^2 - I(I+1)]/[I(2I-1)]$, $I^* = \frac{7}{2}$, $I = \frac{9}{2}$, m^* and m are the magnetic quantum numbers, restricted by $m^* - m = 0, \pm 1$, and δ is the isomer shift.

The results obtained for the hyperfine interaction parameters from these fits are presented in Table I. The fits of the high velocity spectra of KrF_2, α-$[KrF]^+[AsF_6]^-$ and β-$[KrF]^+[AsF_6]^-$ yield accurate values of the quadrupole moment ratio Q_{ex}/Q_{gr}, given in Table I. We give the weighted average

$$Q_{ex}/Q_{gr} = 1.958 \pm 0.002$$

as the best value of this ratio. This value is compared in Table I with the values previously obtained by Kolk[10] from his recalculation of Ruby and Selig's measurements[8] and from Kolk's own measurement on ^{83}Kr in β-hydroquinone.[10]

Our accurate result for Q_{ex}/Q_{gr} was used as a fixed parameter in further fits of the spectra. In these fits the linewidths and the relative line intensities were left free, except in the case of the spectrum of $[KrF]^+[SbF_6]^-$. A meaningful fit of this spectrum could only be obtained after taking the widths of the components as equal and using the average relative intensities derived from the other spectra. These relative line intensities are given in Table II, where they are compared with the theoretical values, obtained as the squares of the appropriate Clebsch–Gordan coefficients, normalized to line 4. The agreement is satisfactory.

The quadrupole coupling strengths are given in Table I. The limits of error include the statistical error of

TABLE I. Hyperfine interaction parameters derived from Mössbauer spectra of krypton compounds.

Compound	Isomer shift (mm/s)	Quadrupole coupling $e^2qQ\,\frac{c}{E\gamma}$ (mm/s)	e^2qQ/h (MHz)	h_p	Q_{ex}/Q_{gr}	Remarks
KrF_2	1.54(4)	129.1(2.2)	978(12)	1.07(2)	1.959(3)	Low velocity
KrF_2	1.57(4)	128.8(2.4)				
α-$KrF^+AsF_6^-$	1.46(10)	141.2(2.0)	1073(8)	1.17(1)	1.955(5)	Low velocity
α-$KrF^+AsF_6^-$	1.67(7)	141.8(1.1)				
β-$KrF^+AsF_6^-$	1.58(5)	140.8(1.0)	1067(8)	1.17(1)	1.958	
$KrF^+SbF_6^-$	1.43(14)	143.8(1.1)	1090(9)	1.19(1)		
KrF_2	1.51(4)	130(7)			2.98(5)	Ruby and Selig,[8] Kolk[10]
Kr in β-hydroquinone	−0.15(3)	1.00(12)			2.05(15)	Kolk[10]

TABLE II. Relative line intensities, normalized to line 4.

Line	KrF_2	α-$KrF^+AsF_6^-$	β-$KrF^+AsF_6^-$	Average	Theoretical value
1	1.16	1.25	1.10	1.17	0.83
2	1.57	1.77	2.03	1.79	1.67
3	1.46	1.07	1.28	1.27	1.17
4	1.00	1.00	1.00	1.00	1.00
5	0.35	0.27	0.24	0.29	0.33
6	1.57	1.70	1.65	1.64	1.55
7	0.95	1.02	0.86	0.94	0.78
8	0.29	0.37	0.12	0.26	0.17
9	1.75	2.92	2.41	2.36	2.00

the fit as well as the calibration error.

The isomer shifts were derived using the position of line 6 of the spectrum, which is close to zero velocity. The unfolded spectra yield accurate values for the $v=0$ point as well as for the small negative shift of line 6 with respect to $v=0$. The isomer shift is obtained by adding to this shift the distance between component (6) and the center of gravity of the spectrum. In this way, most of the calibration error is eliminated from the isomer shift *differences* of the different compounds. These are of more interest to us than the absolute values.

IV. DISCUSSION

In the case of KrF_2, the existence of KrF_2 molecules with linear $D_{\infty h}$ symmetry in the solid has been demonstrated by x-ray diffraction studies.[13] The linearity of KrF_2 is maintained in the vapor as confirmed by infrared and Raman spectroscopy[14] and by electron diffraction studies.[15] No solid state structures of krypton difluoride adducts have yet been investigated by x-ray crystallography, but the existence of fluorine bridges have been clearly established by x-ray crystallography in the case of the analogous xenon difluoride adducts $[XeF]^+[Sb_2F_{11}]^-$[16] and $[XeF]^+[RuF_6]^-$,[17] and the vibrational spectra of a number of analogous krypton difluoride and xenon difluoride adducts of the type $[NgF]^+[MF_6]^-$ and $[NgF]^+[M_2F_{11}]^-$ have been successfully interpreted in terms of molecules containing linear F–Ng–F groups.[5–7,18–21]

The observed Mössbauer parameters can be accounted for qualitatively in terms of the principal contributing valence bond structures:

$$\underset{\text{(Ia)}}{F-Kr^+F^-}, \qquad \underset{\text{(Ib)}}{F^{-+}Kr-F},$$

$$\underset{\text{(IIa)}}{F-Kr^+F-MF_5^-}, \quad \underset{\text{(IIb)}}{F-Kr^+F^-MF_5}, \quad \underset{\text{(IIc)}}{F^{-+}Kr-FMF_5}.$$

In the case of KrF_2, the field gradient possesses axial symmetry (structures Ia and Ib). In addition to structures IIb and IIc, which produce no net *additional* changes in the electric field gradient, structure IIa also becomes an important contributing structure. Its effect is to elongate one Kr–F bond, the bridge bond, and to shorten the other Kr–F bond, the terminal bond, by localization of the electron bond pair in the latter bond, producing an additional increase in the electric field gradient at the krypton nucleus. As the fluoride acceptor strength of the Lewis acid increases, stabilizing valence bond structure IIa with respect to structures IIb and IIc, it might be anticipated that the quadrupole coupling would also increase. While the quadrupole coupling does indeed increase in going from KrF_2 to the adducts, the experimental error is too large to attach any real significance to the difference between quadrupole splittings observed for $[KrF]^+[AsF_6]^-$ and $[KrF]^+[SbF_6]^-$, even though the trend is in the correct direction.

The isomer shifts of the different krypton compounds are determined by the density of the $4s$ electrons at the nucleus. This density is sensitively dependent on the relative participation of the $4p$ and $4s$ electrons in the bonds between krypton and fluorine atoms. A decrease in the number of $4p$ electrons will increase the total s electron density by decreasing the shielding of the $4s$ electrons. Thus, the configuration of krypton in these compounds may be written as $4s^2\,4p^y$, with the number of $4p$ holes being $h_p = 6 - y$. For the linear F–Kr–F groups, the bonding can be assumed to be solely due to p_z electrons transferred from the central Kr atom to the F atoms. In a simple atomic model, the quadrupole coupling strength is proportional to the amount of p_z charge removed from the krypton. Then, the number h_p of p_z holes in the krypton $4p$ shell directly follows from this coupling strength by comparison with the quadrupole coupling for a Kr^+ ion ($h_p = 1$). This latter strength is derived from the atomic beam measurements of Kuiper[22] and of Faust and Chow Shiu[23] on krypton atoms excited to the ^3P-state (electron configuration $4p^5\,5s^1$). These yield a quadrupole coupling constant $(e^2qQ/h) = 904.28 \pm 0.06$ MHz (average of two values). In order to convert this value to that for a Kr^+ ion (^2P state) we use numerical Hartree–Fock calculations for $Kr^+(^2P)$ and $Kr(^3P)$ performed by van Piggelen.[24] His results, $\langle 1/r^3\rangle_{Kr^+} = 16.94$ a.u. and $\langle 1/r^3\rangle_{^3P} = 16.74$ a.u. lead to a value $e^2qQ/h = 915$ MHz for a free Kr^+ ion. Comparison with the measured coupling strengths of the different Kr compounds yields the h_p values given in Table I. Our value for KrF_2 is very close to that found by Ruby and Selig[8] but only because the difference between their and our experimental quadrupole coupling values is canceled by the conversion factor we have applied to $Kr(^3P)$. The validity of van Piggelen's Hartree–Fock results for $\langle 1/r^3\rangle$ can be checked by calculating the quadrupole coupling for the Kr^+ ion, using the value $Q_{gr} = 0.251 \pm 0.005$b of the ^{83}Kr quadrupole moment that was derived by Kuiper[22] from atomic beam measurement without recourse to $\langle 1/r^3\rangle$ calculations. We find $e^2qQ_{gr}/h = \frac{4}{5}e^2Q_{gr}\langle 1/r^3\rangle = 798 \pm 16$ MHz, which is 13% less than the experimental value. Compared with the general degree of consistency between calculated and measured quadrupole couplings, recently discussed by Lindgren[25], this is acceptable. Better agreement might be expected when polarization and correlation effects are taken into account in the calculations, but this is not a simple matter.

The value $h_p = 1.07 \pm 0.02$ obtained for KrF_2 on the

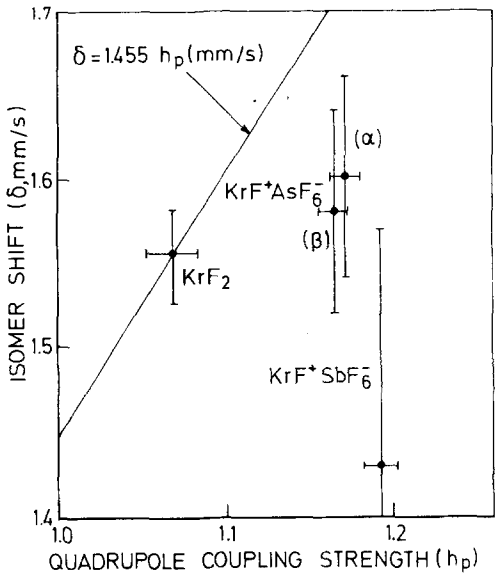

FIG. 2. Plot of isomer shift of krypton compounds vs reduced quadrupole coupling strength $[h_R = (eq^2Q)\exp/(e^2q^2Q)_{at}]$.

basis of our atomic model is larger than the value $h_p = 0.94$ reported by Schreiner *et al.*,[11] as a result of an NMR measurement. The difference of the two values, which is of the order of 10%, probably reflects the limits of validity of the simple model used.

A linear relationship should be expected between the number of p holes derived from the quadrupole coupling and the isomer shift on the basis of the simple atomic model. Such a relation has, for instance, been observed for a large number of iodine compounds.[26] For the krypton compounds, we have also attempted to correlate h_p with the isomer shift, using $\delta = 1.455 h_p$, deduced from the case of KrF_2. We see from Fig. 2 that the increase of δ with h_p does not occur for the $KrF_2 \cdot MF_5$ compounds, but rather, within the limits of error, there may even be a slight decrease of δ with increasing h_p.

The closely similar isomer shifts combined with the calculated values of h_p that are not far from unity are consistent with the valence bond representation of KrF_2 (structures Ia and b) and F–Kr–F–MF_5 (structures IIa–c) which place a single formal positive charge on krypton (i.e., one Kr $4p$ electron is transferred to two fluorines).

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†On leave from Soreq Nuclear Research Centre, Yavne, Israel.

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